

(12)

**EUROPEAN PATENT APPLICATION**

(21) Application number: **89810306.4**

(51) Int. Cl. 4: **D 06 P 5/08**  
**D 06 P 1/52, C 11 D 17/00**

(22) Date of filing: **25.04.89**

(30) Priority: **27.04.88 DE 3814208**

(43) Date of publication of application:  
**08.11.89 Bulletin 89/45**

(84) Designated Contracting States:  
**BE CH DE ES FR GB IT LI NL**

(71) Applicant: **SANDOZ AG**  
**Lichtstrasse 35**  
**CH-4002 Basel (CH)**

(84) Designated Contracting States:  
**BE CH ES FR GB IT LI NL**

(71) Applicant: **SANDOZ-PATENT-GMBH**  
**Humboldtstrasse 3**  
**D-7850 Lörrach (DE)**

(84) Designated Contracting States: **DE**

(72) Inventor: **Pavan, Gino**  
**Bärenfelsweg 10**  
**CH-4147 Aesch (CH)**

**Robinson, Tibor**  
**Gellertstrasse 45**  
**CH-4052 Basel (CH)**

**Sanahuja, Viktor**  
**Therwilerstrasse 63**  
**CH-4153 Reinach (CH)**

(54) **A dye scavenger.**

(57) A process for preventing discoloration of a textile material comprising washing one or more dyed textile materials (herein defined as "the wash") that contain free dye or liberatable dye (i.e. dye that can be washed out of the material) in the presence of a dye scavenger (for taking up any free dye or any dye that is liberated in the wash) the scavenger comprising a substrate to which a polymeric material (hereinafter referred to as the polymeric material) selected from any one of Products A to D is applied, where Products A to D, are as follows:

(A) a polymeric reaction product of a monofunctional or polyfunctional amine having one or more primary and/or secondary tertiary amino groups with cyanamide, dicyandiamide (DCDA), guanidine or bisguanide where up to 50% of cyanamide, dicyandiamide, guanidine or bisguanide may be replaced by a dicarboxylic acid or a mono- or di-ester thereof, said product (A) containing at least one free hydrogen atom linked to a nitrogen atom (hereinafter referred to as Product A); or

(B) a water soluble polymeric reaction product of (A) with an epihalohydrin or a precursor thereof, (hereinafter referred to as Product B); or

(C) a water soluble homopolymer of a mono- or di-allyl amine, or a copolymer of mono- and di-allylamine, in which

at least one N atom is capable of forming an acid addition salt and/or at least one N atom is an ammonium group (hereinafter referred to as Product C); or

(D) a water soluble copolymer, of a mono- and/or di- and/or triallylamine with a copolymerisable monomer, in which at least one N atom is capable of forming an acid addition salt and/or at least one N atom is a quaternary ammonium group (hereinafter referred to as Product D); or a mixture of one or more of Products A to D.

**EP 0 341 205 A2**

## Description

## A DYE SCAVENGER

One problem that arises with dyed material that contains either free dye or dye that is not sufficiently well bound to the material is that it is not retained in the material during a conventional household washing procedure, that is to say the free or insufficiently well bound dye is liberated and can therefore be taken up by other substrates, (which may be dyed or undyed) thereby affecting the colour or indeed causing colouring of these other substrates.

To alleviate this problem, there is provided according to the invention, a process for reducing or preventing discoloration of a textile material in a wash bath, comprising

washing one or more dyed textile materials (herein defined as "the wash") that contain free dye or liberatable dye (i.e. dye that can be washed out of the material) in the presence of a dye scavenger capable of taking up any free dye or any dye that is liberated in the wash, the scavenger comprising a substrate to which a polymeric material, (hereinafter referred to as the polymeric material) selected from any one of Products A to D, is fixed where Products A to D are as follows:

(A) a polymeric reaction product of a mono-functional or polyfunctional amine having one or more primary and/or secondary tertiary amino groups with cyanamide, dicyandiamide (DCDA), guanidine or biguanide where up to 50% of cyanamide, dicyandiamide, guanidine or biguanide may be replaced by a dicarboxylic acid or a mono- or di-ester thereof, said product (A) containing at least one free hydrogen atom linked to a nitrogen atom (hereinafter referred to as Product A); or

(B) a water soluble polymeric reaction product of (A) with an epihalohydrin or a precursor thereof, (hereinafter referred to as Product B); or

(C) a water soluble homopolymer of a mono- or di-allyl amine, or a copolymer of mono- and di-allylamine, in which at least one N atom is capable of forming an acid addition salt and/or at least one N atom is an ammonium group (hereinafter referred to as Product C); or

(D) a water soluble copolymer, of a mono- and/or di- and/or triallylamine with a copolymerisable monomer, in which at least one N atom is capable of forming an acid addition salt and/or at least one N atom is a quaternary ammonium group (hereinafter referred to as Product D); or a mixture of one or more of Products A to D.

The dye scavenger may be dyed or undyed. Preferably the scavenger is undyed.

Preferably the polymeric material of the dye scavenger has a molecular weight of over 4000, more preferably over 5000.

Product A is known, and is described for example in British Published Patent Application No 2 142 642, US Patent 4 764 585 and US Patent 4 410 652, and may be prepared by methods described in said

patents, the contents of which are incorporated herein by reference.

Suitably the amine, in free base or salt form, is reacted with the other starting material in the absence of water at elevated temperatures optionally in the presence of a non-aqueous solvent. Preferably the reaction is carried out in the absence of solvent at a temperature of 140-160°C, and for most combinations of reagents, ammonia is evolved. The reagents are preferably reacted in a molar ratio of 0.1 to 1 mole of cyanamide, DCDA, guanidine or biguanide per mole of reactive -NH- or -NH<sub>2</sub> group, and when DCDA is reacted with a polyalkylene polyamine, the molar ratio of the reactants is more preferably from 2:1 to 1:2, particularly about 1:1. Preferably the reactants are reacted in the presence of a catalyst selected from metals, metal salts and heterocyclic nitrogen-containing compounds (defined as catalyst K in USP 4 764 585).

The Products A are near-colourless viscous liquids or solids which are basic in character, water-soluble either in the free base or salt form, and contain reactive hydrogen atoms bonded to nitrogen.

Up to 50 mole % preferably up to 20 mole % of the DCDA or other reagent to be reacted with the amine may be replaced by a dicarboxylic acid or a mono- or di-ester thereof. Suitable acids include adipic acid, oxalic acid and terephthalic acid, for example in the form of their dimethyl esters.

Particularly preferred Products A are the reaction products of DCDA with diethylenetriamine or triethylenetetramine, preferably in the presence of a catalyst selected from metals, metal salts and heterocyclic nitrogen containing compounds (especially zinc chloride) defined as catalyst K in USP 4 764 585.

Product B is described in USP 4,439,203 the contents of which are incorporated herein by reference.

Products C and D are described in Japanese Kokai:-

51-57 793 ; 56-9999 ; 56-53 292 ; 56-134 284 ; 57-11 288 ; 57-591 ; 57-92 012 ; 60-7079 ; 45-1457 and 49-31 631 ;

the contents of which are incorporated herein by reference.

Further products of Product C and D are described in EP 280,655, the contents of which are incorporated herein by reference as well as D.O.S. 37 205 08.

Preferably the polymeric material is Product A, C, or D.

More preferably the polymeric material of the scavenger is Product A or Product C'; where Product C' is a synergistic mixture containing as active ingredient a textile auxiliary (T) and the polymeric compound (P) in which T is the product of a 2-step reaction comprising the steps of

1) reacting an epihalohydrin with aqueous ammonia at 50-90°C in an initial mole ratio of 4 moles epihalohydrin to 8 to 10 moles of

ammonia and

2) reacting the product of step 1, after removal of excess ammonia, with a further 0.1 to 0.5 moles of epichlorohydrin; and

P is a water soluble homopolymer of a mono- or di-allylamine, or a water soluble copolymer comprising (preferably consisting of) mono-, di- or tri-allylamine units.

Such a product is described in EP 280,655 (= US Serial No. 07/151,032)

The synergistic mixture may also contain 3) the reaction product of epichlorohydrin or a precursor thereof with a polyalkylene polyamine.

Most preferably the polymeric Product is Product A (especially Product of Example 1 as described in USP 4 764 585).

The amount of polymeric material to substrate of scavenger is to 20 %, more preferably 2 to 6 %, by weight of substrate.

The scavenger can be in any form. The polymeric material can be applied to the whole substrate or to just a surface. Preferred substrates including fabrics, garments, films, non-woven material or paper.

The substrates can be natural or synthetic, preferably undyed cotton, undyed regenerated cellulose or undyed natural or synthetic polyamide.

The substrates can be treated with any one of Products A to D by known methods, for example by immersion, padding, spraying, printing, exhaustion. The amount used is preferably from 2 to 200 g/l, more preferably 10 to 80 g/l (based on the activates of components A to D) preferably in a goods to liquor ratio of 1:1 to 1:30.

The scavenger that is so produced can be used in standard washing procedures, merely by being added to the wash. The scavenger takes up any free or liberated dyestuff, in particular anionic dyestuff, free in the bath. In this way, the scavenger assists in preventing staining of the washing by free dye being taken up undesirably on other pieces in the wash. The scavenger is optimally effective with dyeings, preferably of not more than 1/1 standard depth, especially in light shades.

The amount of scavenger should be sufficient to prevent as reduce staining and/or discoloration. This amount will vary depending on the total amount of wash and also on the properties of wash that contains free or liberatable dye.

The amount of scavenger to the wash is preferably 5 to 80 g to 1 kg of the wash; more preferably 10 to 30 g to 1 kg of wash.

Preferably the substrate of scavenger is a textile material.

In this specification, unless indicated to the contrary reference to Products A to D includes reference to mixtures thereof.

The invention will now be illustrated by the following Examples in which all parts of percentages are by weight and all temperatures are in °C unless indicated to the contrary.

#### Example 1.

A fabric of 100 % cotton is impregnated by padding (squeezed to 80 % dry weight) with 60 g/l of the product of Example 1 of US Patent 4,764,585 (=

D.O.S 35,25,104) - calculated on 100 % active substance-and this is dried at 100°C. The textile material (hereinafter referred to as the "scavenger") is then added to a household coloured wash made up of cotton textile fabric dyed with C.I. Reactive Violet 23 and undyed cotton textile fabric. The weight of the wash is 3 kg and the wash to bath ratio is 1:4. The washing powder used was "Omo", a commercially available product, for a 60°C wash and was used in an amount of 6 g/l.

The amount (by weight) of scavenger to washing is about 1 that is to say 30 g of scavenger is used.

The wash and scavenger is then washed in a Bauknecht washing machine, a commercially available household machine, at 60 °C and is then dried.

After drying it can be seen that the dye scavenger has taken up dye from the insufficiently fast dyeing.

#### Example 2

Example 1 is repeated, using instead of the C.I. Reactive Violet 23, C.I. Direct Blue 251. The resulting scavenger is soiled with free dye.

#### Example 3

A dye scavenger is prepared using the polymeric product of Example 1 of GB 2,192,893 A (= D.O.S. 3'720'508)

Example 1 is repeated using the following wash.

60-70 % cotton dyed with C.I. Direct Blue 251 ;

10 % nylon dyed with the dye of Example 1 of D.O.S. 2,400,654 ;

15 % Dacron T56, dyed with C.I. Disperse Yellow 23 ;

and

5 % Orlon dyed with C.I. Basic Blue 45.

The wash is then washed with the scavenger at 60°C. The scavenger picks up the free dye available (primarily of C.I. Direct Blue 251) whereas the fabrics of the wash retain their clear colours.

In all the Examples there is substantially no or very little soiling of the other fabrics of the wash than the scavenger by free or liberated dye.

#### Claims

1. A process for reducing or preventing discoloration of a textile material in a wash bath comprising

washing one or more dyed textile materials (herein defined as "the wash") that contain free dye or liberatable dye (i.e dye that can be washed out of the material) together with a textile material that can be discolored in the presence of a dye scavenger (for taking up any free dye or any dye that is liberated in the wash) the scavenger comprising a substrate to which a polymeric material (hereinafter referred to as the polymeric material) selected from any one of Products A to D, is applied where Products A to D are as follows:

(A) a polymeric reaction product of a mono-functional or polyfunctional amine having one or more primary and/or secondary tertiary amino groups with cyanamide, dicyandiamide (DCDA), guanidine or bisguanide where up to

50% of cyanamide, dicyandiamide, guanidine or bisguanide may be replaced by a dicarboxylic acid or a mono- or di-ester thereof, said product (A) containing at least one hydrogen atom linked to a nitrogen atom (hereinafter referred to as Product A); or

(B) a water soluble polymeric reaction product of (A) with an epihalohydrin or a precursor thereof, (hereinafter referred to as Product B); or

(C) a water soluble homopolymer of a mono- or di-allyl amine, or a copolymer of mono- and di-allylamine, in which at least one N atom is capable of forming an acid addition salt and/or at least one N atom is an ammonium group (hereinafter referred to as Product C); or

(D) a water soluble copolymer, of a mono- and/or di- and/or triallylamine with a copolymerisable monomer in which at least one N atom is capable of forming an acid addition salt and/or at least one N atom is a quaternary ammonium group (hereinafter referred to as Product D); or a mixture of one or more of Products A to D.

2. A process according to Claim 1 in which the dye scavenger is undyed.

3. A process according to Claim 1 or Claim 2 in which the molecular weight of the polymeric material of the dye scavenger is over 4000.

4. A process according to any one of the preceding claims in which the polymeric material is Product A.

5. A process according to any one of the preceding claims in which the polymeric product is the reaction product of diethylene triamine or triethylene tetraamine with DCDA

reacted at an elevated temperature in the presence of a catalyst selected from metals, metal salts and heterocyclic nitrogen-containing organic bases.

6. A process according to Claim 5 in which the catalyst is zinc chloride.

7. A process according to any one of the preceding claims in which the polymeric material is a synergistic mixture containing as active ingredient a textile auxiliary (T) and the polymeric compound (P) in which T is the product of a 2-step reaction comprising the steps of

1) reacting an epihalohydrin with aqueous ammonia at 50-90°C in an initial mole ratio of 4 moles epihalohydrin to 8 to 10 moles of ammonia and

2) reacting the product of step 1, after removal of excess ammonia, with a further 0.1 to 0.5 moles of epihalohydrin and

P is a water soluble homopolymer of a mono- or di-allylamine, or a water soluble copolymer comprising mono-, di- or tri-allylamine units.

8. A process according to Claim 7 in which the polymeric material also contains 3) the reaction product of epichlorohydrin or a precursor thereof with polyalkylene polyamine.

9. A process substantially as herein defined with reference to any one of the Examples.

10. The use of a scavenger defined in any one of the preceding claims for reducing or preventing discoloration of a textile material in a wash bath.

40

45

50

55

60

65

4

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 341 205 A3**

(12)

**EUROPEAN PATENT APPLICATION**

(21) Application number: 89810306/4

(51) Int. Cl.<sup>5</sup>: **D06P 5/08, D06P 1/52,  
C11D 17/00**

(22) Date of filing: 25.04.89

(30) Priority: 27.04.88 DE 3814208

(43) Date of publication of application:  
08.11.89 Bulletin 89/45(84) Designated Contracting States:  
BE CH DE ES FR GB IT LI NL(88) Date of deferred publication of the search report:  
08.05.91 Bulletin 91/19(71) Applicant: **SANDOZ AG**  
Lichtstrasse 35

CH-4002 Basel(CH)

(84) BE CH ES FR GB IT LI NL

Applicant: **SANDOZ-PATENT-GMBH**  
Humboldtstrasse 3  
W-7850 Lörrach(DE)

(84) DE

(72) Inventor: **Pavan, Gino**  
Bärenfelsweg 10

CH-4147 Aesch(CH)

Inventor: **Robinson, Tibor**

Gellertstrasse 45

CH-4052 Basel(CH)

Inventor: **Sanahuja, Viktor**

Therwilerstrasse 63

CH-4153 Reinach(CH)

(54) **A dye scavenger.**

(57) A process for preventing discoloration of a textile material comprising

washing one or more dyed textile materials (herein defined as "the wash") that contain free dye or liberatable dye (i.e. dye that can be washed out of the material) in the presence of a dye scavenger (for taking up any free dye or any dye that is liberated in the wash) the scavenger comprising a substrate to which a polymeric material (hereinafter referred to as the polymeric material) selected from any one of Products A to D is applied, where Products A to D, are as follows:

(A) a polymeric reaction product of a monofunctional or polyfunctional amine having one or more primary and/or secondary tertiary amino groups with cyanamide, dicyandiamide (DCDA), guanidine or bisguanide where up to 50% of cyanamide, dicyandiamide, guanidine or bisguanide may be replaced by a dicarboxylic acid or a mono- or di-ester thereof, said product (A) containing at least one free hydrogen atom linked

to a nitrogen atom (hereinafter referred to as Product A); or

(B) a water soluble polymeric reaction product of (A) with an epihalohydrin or a precursor thereof, (hereinafter referred to as Product B); or

(C) a water soluble homopolymer of a mono- or di-allyl amine, or a copolymer of mono- and di-allylamine, in which at least one N atom is capable of forming an acid addition salt and/or at least one N atom is an ammonium group (hereinafter referred to as Product C); or

(D) a water soluble copolymer, of a mono- and/or di- and/or triallylamine with a copolymerisable monomer, in which at least one N atom is capable of forming an acid addition salt and/or at least one N atom is a quaternary ammonium group (hereinafter referred to as Product D); or a mixture of one or more of Products A to D.

**EP 0 341 205 A3**



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 89 81 0306

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	GB-A-2099007 (SANDOZ) * the whole document *	1, 2, 4-6, 8	D06P5/08 D06P1/52 C11D17/00 D06P5/06
Y		7	
D	& US-A-4439203 ---		
Y	EP-A-142337 (NITTO BOSEKI CO. LTD.) * abstract * -----	7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			D06P
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 26 FEBRUARY 1991	Examiner DELZANT J-F.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	